FINAL REPORT

EXPERIMENT STUDY OF REACTIVITY AND MORPHOLOGICAL CHANGE OF CAO-BASED CHEMICAL LOOPING PARTICAL IN CYLIC CARBONATION-CALCINATIOIN REACTIONS

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Abstract

The essence of The Ohio State University (OSU) Chemical Looping Processes (CLPs) is cyclic gas-solid reaction. CaO-based cyclic reaction is one of the basic OSU CLPs. Reactivity and recyclability of solid reactants are two major issues which are deteriorated through the morphological properties of solid reactants in the cyclic CaO-CO_2 reactions. Particle development is mostly focused on optimizing fresh morphological and anti-sintering properties. The goal of this study is to investigate the deactivation mechanism of CaO-based calcium looping particles. The reactivity of "Fresh CaO" and "Sintered CaO" are compared through varying reaction time to study the effect of time on the resulting particle reactivity. The effect of reaction temperature on CaO is studied by comparison between 700℃ and 800℃ sintering in Thermo Gravimetric Analyzer (TGA). Through comparing the CO_2 capture capacities, the surface area and pore volume of CaO after three and six reaction cycles with Surface Area & Pore Size Analyzer (BET), the effects of cyclic CaO-CO_2 reactions can be found. Ionic diffusion through the calcite layer during the reaction of CaO and CO_2 is also studied through analyzing the cross-section area of partially-reacted CaO tablets through the Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray analysis. The data shows that, non-structural ion (CO_3^{2-}) is the dominating ion in the CaO-CO_2 cyclic reactions and particle development should focus on improving the initial morphological properties. Cyclic reaction is an independent factor which deactivates solid reactivity, which is against the understanding that solid deterioration was almost unanimously caused by the sintering effect in the previous studies.

Keywords: ionic diffusion, multiphase reactions, inert marker experiment, interface, particle formation, environment

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Introduction

The Chemical Looping Processes (CLPs) developed in The Ohio State University (OSU) can enhance H_2 production with 100% CO_2 capture. Currently, there are two types of CLPs under intensive study in The Ohio State University: Coal Direct Chemical Looping (CDCL) and Syngas Chemical Looping (SCL). The essence of OSU CLPs is cyclic gas-solid reaction, in which solid reactants capture and release gas molecules in each cyclic reaction step. OSU CLPs are CaO-based and Fe-based cyclic reactions basically.

In CaO-based reaction, CaO releases and captures partial or whole CO_2 molecules in each carbonation-calcination step. Two consecutive steps are included in the CO_2-capture reaction: the surface chemical-reaction-controlled step and the solid-phase-ionic-transfer-controlled step. In chemical engineering, there is intensive ongoing research of using CaO as sorbent to capture CO_2 for sequestration[7,15,4].

Equation 1: $$CaO_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3(s)}$$

During the calcite formation via the reaction of CaO and CO_2, there first forms a thin layer of $CaCO_3$ on the CaO solid-grain surface. Since $CaCO_3$ has higher molar volume (36.9 cm^3/g) than CaO (16.7 cm^3/g), the formed product layer would cover the solid surface and hinder the direct contact of CaO and CO_2. Further solid conversion has to proceed through solid-phase ionic diffusion. This ionic diffusion process can be dominated by: 1) inward diffusion mode: counter-current diffusion of inward CO_3^{2-} anion groups and outward O^{2-} anions, 2) outward diffusion mode: outward co-current diffusion of Ca^{2+}cations and O^{2-} anions, or 3) mixed diffusion mode: the combination of both processes 1 & 2 (see Figure 1)[19].

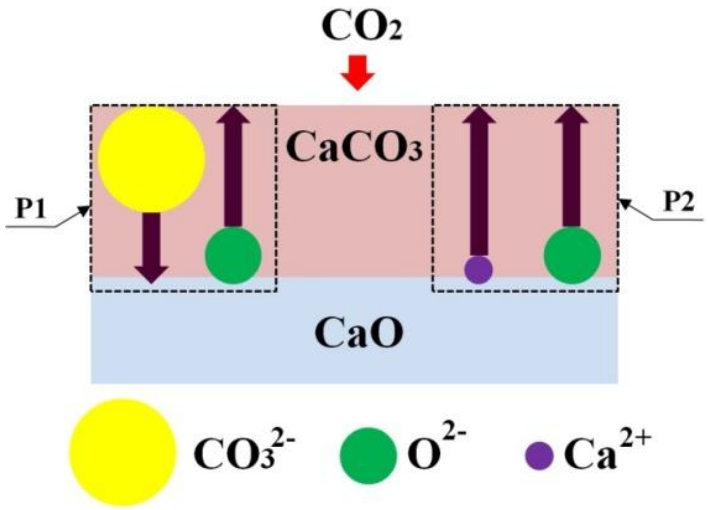

Figure 1: Illustration of the two competing ionic diffusion processes in the reaction of CaO and CO_2

CO_2 first reacts with CaO on its surface and converts through the product ($CaCO_3$) layer. The structural ion Ca^{2+} in $CaO/CaCO_3$ is not changed by the inward and outward diffusion of the non-structural ion CO_3^{2-} in $CaO/CaCO_3$. After the surface of CaO is fully covered by $CaCO_3$, further conversion continues through CO_2-derived ionic diffusion. The ion transfers and/or exposes solid reactant to the CO_2- $CaCO_3$ interface. Since both the CaO exposure to the CO_2 and the width of the ionic diffusion pathway are determined by the surface and pores structure, solid of morphology properties effect the CaO-CO_2 reaction significantly.

From a variety of reports, these properties are likely to deteriorate with cyclic reactions in progress, especially in high-temperature applications. Almost all the essays published so far insists that the deterioration and the reducing reactivity of CaO morphological properties are both due to the particle sintering at high temperature. Small particles aggregate together into big ones. In this study, longer exposure to high-temperature is more likely to deteriorate and reduce the reactivity of CaO. It is conditional that higher temperature has a crucial negative effect on the

CaO’s morphological properties and reducing reactivity. The CaO reactivity might be reduced more slowly if structural ions participate in ionic diffusion at a higher temperature.

Theory of inert marker experiment

Inert marker experiment is used to investigate the ionic diffusion mechanism during the cyclic CaO-CO_2 reactions[13,12,9,16,17]. A piece of inert material (Pt in this study) is placed on the top surface of CaO tablet as a tracer. Since material Pt does not dissolve into either CO_2 gas phase or CaO tablet, it could be used as a marker of the initial interface of cyclic CaO-CO_2 reactions. As shown in Figure 2 (a), a very thin layer of Pt was pasted on the top surface of CaO tablet. The ionic diffusion mechanism could be determined by the final location of the Pt marker layer. If the Ca^{2+} cations and O^{2-} anions co-diffuse faster, the product $CaCO_3$ layer will be on the top of the Pt inert marker layer, which means the inert maker layer stays at interface of the product and original layers (see Figure 2(b)). If the outward Ca^{2+} cations and O^{2-} anions have a slower diffusing rate than that of counter-current diffusion of inward CO_3^{2-} anion groups and outward O^{2-} anions. The $CaCO_3$ product layer is formed underneath the inert maker Pt layer as shown in Figure 2 (d). If two processes have a comparable diffusion rate, the inert marker layer will be located inside of the formed $CaCO_3$ (see Figure 2 (c)). Therefore, through finding the eventual location of the inert marker Pt layer, the ionic diffusion mechanism in the CaO-CO_2 reaction could be studied.

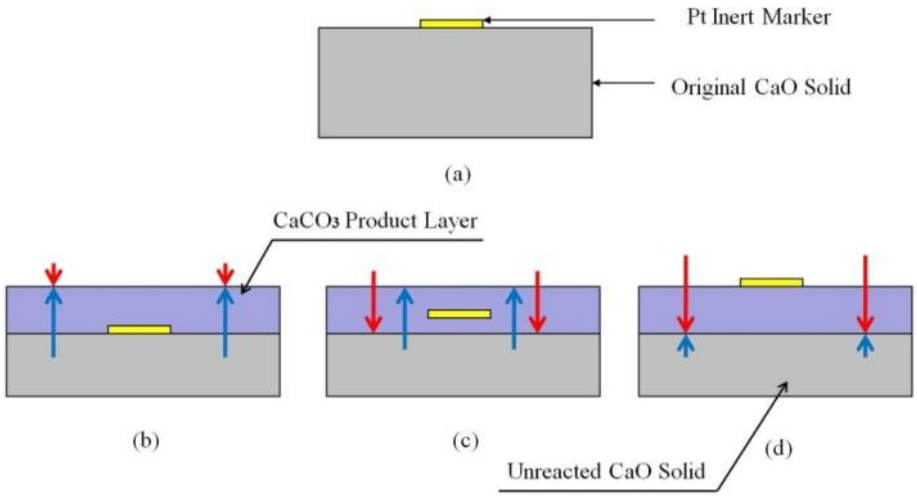

Figure 2: Principle of inert marker experiment. (a) the original CaO solid with an inert marker (platinum in this study); (b) outward diffusion mode; (c) mixed diffusion mode; (d) inward diffusion mode.

Experimental Procedures

Materials

Graymount offers the Naturally-occurring limestone power ($CaCO_3$). CaO powder was 99.95% pure from Aldrich Chemistry. 99.99% purity of CO_2 and N_2 were used in this study.

Tests of ionic diffusion through calcite ($CaCO_3$) layer during the reaction of CaO and CO_2

Similar to the previous studies, cylindrical tablets (Diameter≈ 6mm, Height≈4mm) were pelletized with purchased CaO powder by 5 MPa pressure[10]. The new made tablets were then sintered at 1200℃ with 99.99% CO_2 for 3000 minutes in Thermo Gravimetric Analyzer (TGA). 1200℃ was chosen as sintering temperature for removing voids in the dense pellet, therefore, gas phase CO_2 could barely diffuse into the CaO pellet during the further repeated carbonation reactions. After TGA was cooled to room temperature, a very thin layer of Pt was placed on the top surface of the tablets immediately. Then, the tablets were transferred to a horizontal tubular furnace fast and heated up to 650℃ under 99.99% N_2 for about 4 months. After that, those tablets were mounted into epoxy resin and cut diagonally with the Pt layer as shown in Figure 3. The cutting cross surface area was polished for further Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) analyses. Partially reacted CaO samples were analyzed by X-ray Diffraction (XRD) for experimental results support.

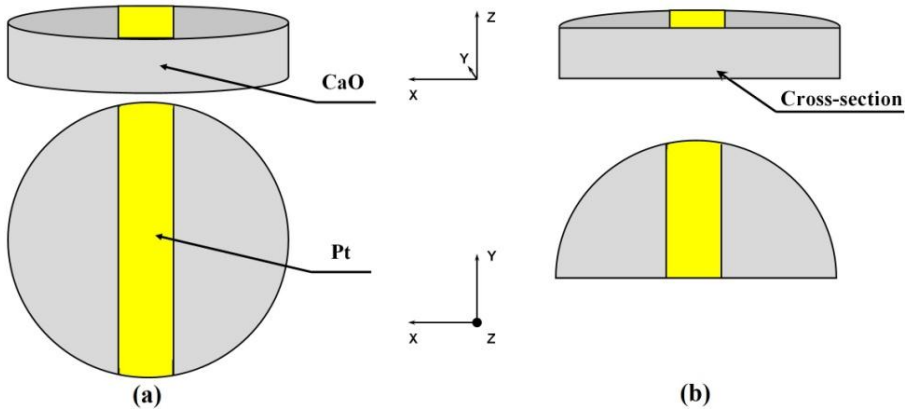

Figure 3: (a) illustration of the layout of Pt layer on the CaO tablet; (b) illustration of the half tablet after the diagonal cutting.

Tests of the effects of reaction temperature, reaction time, and carbonation-calcination cycles on the resulting reactivity of CaO solid

Limestone power ($CaCO_3$) and 99.99% pure N_2 will be used. Around 30 mg limestone powder was used to prepare CaO solid, which will be made and tested by Perkin-Elmer (Pyris 1) Thermo Gravimetric Analyzer (TGA) apparatus. A total mixture gas of 10 % CO_2 and 90 % N_2 at 120 ml min^{-1} was used for the final carbonation reaction (γ section in Figure 4). The five sintering samples needed and their gas composition needed during the reaction (α and β sections in Figure 4) are listed in Table 1. Temperature 650℃ is used to measure all the samples' final relativities after α and β sessions at both 700℃ and 800℃. Their CO_2 capture capacities can be tested by weight capture percentage at 30 min with TGA, and the surface area and pore volume of the five samples will be tested by BET as shown in Table 2. All the samples' preparation details could be found in Table 2 and Figure 4.

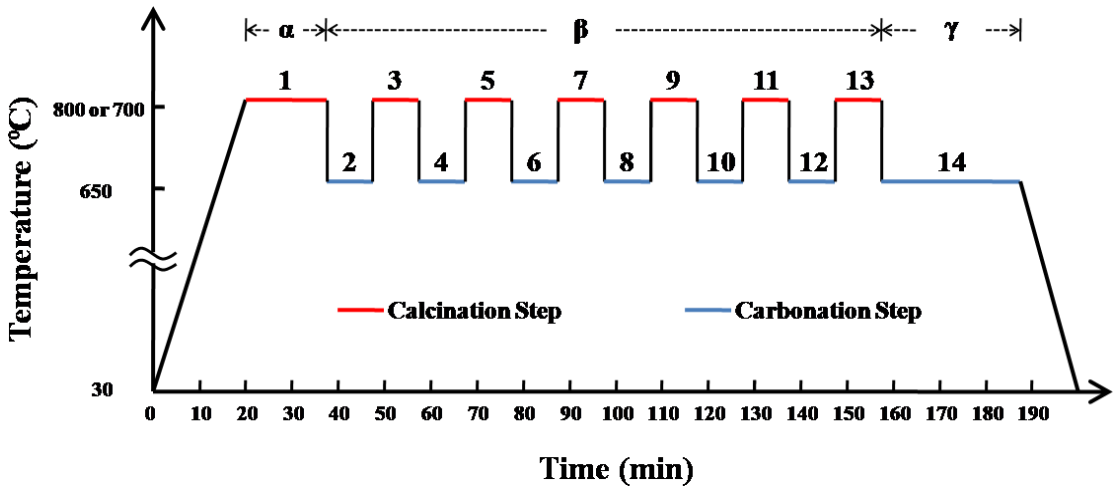

Figure 4: Schematic illustration of temperature sequence of CaO sample preparation and test. (α: initial calcination; β: CCR cycles; γ: final test).

Table 1: Detailed information about the preparation procedures of all the CaO samples prior to the final CO_2 capture capacity tests.

Sample I.D.	Initial Calcination (α)		Carbonation-Calcination Reaction (CCR) Cycles (β)			
	Calcination Time	Calcination Gas	Calcination Step Time (each)	Carbonation Step Time (each)	N_2 Introduced Steps	CO_2+N_2 Introduced Steps
Fresh CaO	Stops after calcination completes	100 % N_2	N/A	N/A	N/A	N/A
Sintered CaO (Sintering + 0 CCR)	20 min	100 % N_2	10 min	10 min	2 ~ 13	N/A
Sintering + 3 CCR	20 min	100 % N_2	10 min	10 min	2, 3, 5, 6, 7, 9, 10, 11, 13	10 % CO_2 @ 4, 8, 12
Sintering + 6 CCR	20 min	100 % N_2	10 min	10 min	3, 5, 7, 9, 11, 13	10 % CO_2 @ 2, 4, 6, 8, 10, 12
Sintered $CaCO_3$	20 min	100 % CO_2	10 min	10 min	13	100 % CO_2 @ 2 ~ 12

Table 2: Morphological information of the CaO solid reactants

Sample I.D.	Surface Area (m^2/g)	Pore Volume (cc/g)
Fresh CaO @ 800 ^oC		
Sintered CaO (Sintering + 0 CCR) @ 700 ^oC		
Sintered CaO (Sintering + 0 CCR) @ 800 ^oC		
Sintering + 3 CCR @ 800 ^oC		
Sintering + 6 CCR @ 800 ^oC		
Sintered $CaCO_3$ @ 800 ^oC		

To research on the effect of time, the reactivity of "Fresh CaO" and "Sintered CaO" are compared through varying reaction time. The "Fresh CaO" can be obtained right after fulfilled calcinations of $CaCO_3$. However, the "Sintered CaO" ("sintering+ 0 CCR") sample will be obtained after sintering under an extended cyclic temperature under 99.99% N_2 environment which does not have any gas reactants involved.

The effect of reaction temperature on CaO is studied by comparison between 700℃ and 800℃ sintering in the TGA. With other variables held constant, the only factor which results in reactivity difference in the previous step is temperature. CaO weight capture percentage will be tested at the same condition (650℃).

In order to study the effect of cyclic CaO-CO_2 reactions, reaction temperature and time are both fixed. Three and six cyclic carbonation-calcinations reactions of CaO will be conducted in the same reaction time as that of "Sintered CaO". Therefore, the number of carbonation-calcinations cycles will be only variable. Same as previous steps, through comparing CO_2

capture capacities, surface area and pore volume, effects of cyclic $CaO\text{-}CO_2$ reactions can be achieved.

Results and discussion

Ionic diffusion through calcite ($CaCO_3$) layer

The SEM result is shown in Figure 5. As illustrated in Figure 5(a), the Pt layer is finally located on the top surface of $CaO/CaCO_3$ solid phase. To further identify the final result, mappings of Pt, Ca, and C are achieved from an EDS experiment (see Figure 5 (b), (c) and (d)). It further proves that the original CaO and the formed $CaCO_3$ solid phase are underneath the Pt layer, which matches the inward diffusion mode. In other words, the CO_3^{2-} anion groups diffuse inward into the solid phase and the O^{2-} anions diffuse outward to the solid surface. The CO_3^{2-} anions groups diffuse inwardly to react with Ca^{2+} to form $CaCO_3$ at the $CaCO_3$/CaO interface. At the same time, CO_2 reacts with the outward diffusing O^{2-} anions to form CO_3^{2-} anions. Since both CO_3^{2-} anion groups and O^{2-} anions have two negative charges, the molar ratio of both diffusing ions is 1:1 to make maintain charge balance in the local phase. Bhatia and Perlmutter[3] (1983) proved part of this mechanisms experimentally and Anderson's work[2] missed the possible mixed diffusion mode in 1968.

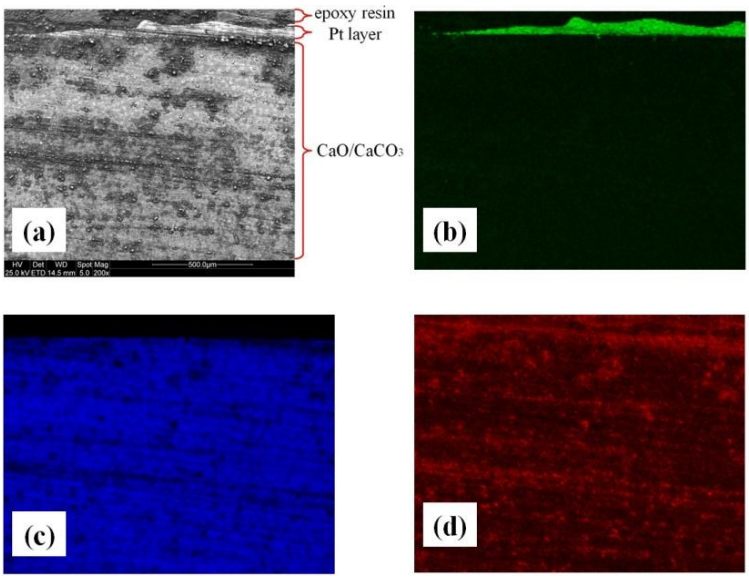

Figure 5: (a) SEM micrograph of the cross-sectional area; (b) Pt mapping; (c) Ca mapping; (d) C mapping.

Partially carbonated CaO was analyzed with X-ray Diffraction (XRD) to further approve the experimental work (see Figure 6). As illustrated this figure, partially carbonated CaO sample consists of the un-reacted CaO and $CaCO_3$ structure and the new formed $CaCO_3$ is in calcite structure.

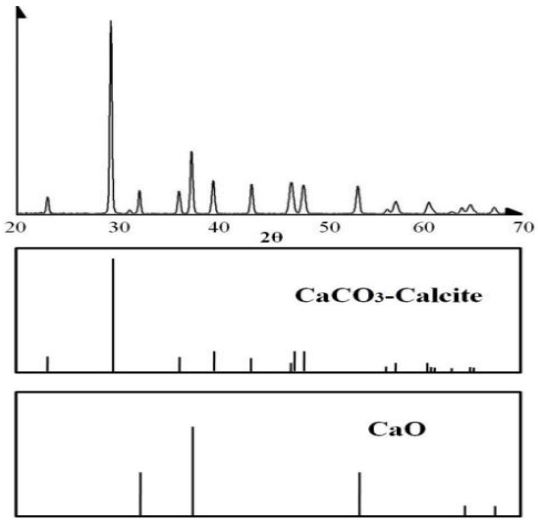

Figure 6: X-ray diffraction pattern of the partially reacted CaO solid sample.

Effect of Reaction Time

To study the effect of time, the time length of solid's exposure is varied at different reactions. Two samples, "Fresh CaO" and "Sintered CaO" ("Sintering + 0 CCR") are used for comparison. CO_2 capture capacities (30 min weight capture percentage) of the both samples are tested at the same gas environment and temperature (650 ℃). As shown in Figure 7 (a), the "Sintered CaO" ("Sintering + 0 CCR") has lower weight capture percentage than the "Fresh CaO" at the same reaction conditions. In other words, "Sintered CaO" ("Sintering + 0 CCR") has lower reactivity than "Fresh CaO".

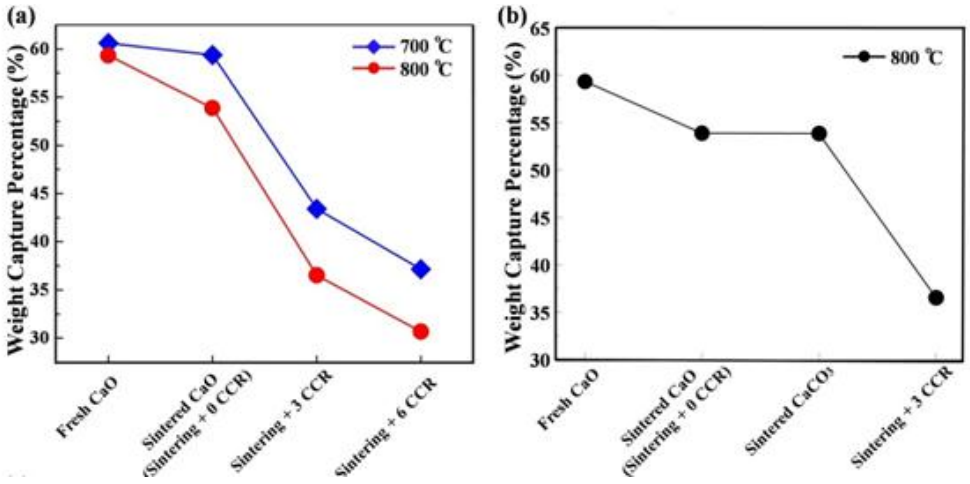

Figure 7: Effects of reaction time, reaction temperature, and cyclic reactions on the CO_2-capture capacities (reactivities) of CaO. ((a): 30 min CO_2 weight capture percentage of CaO; (b): control test of sintered $CaCO_3$)

With longer reaction time, smaller gains/particles are agglomerated and pores "fused" to a higher extent by sintering, which causes a greater deteriorating effect on CaO particles. The particles' lower surface area and pore volume reflect additional effects from sintering (see Table 3).

Table 3: Morphological information of the "Fresh CaO" and "Sintered CaO"

Sample I.D.	Surface Area (m^2/g)	Pore Volume (cc/g)
Fresh CaO @ 800 ^oC	18.576	0.134
Sintered CaO (Sintering + 0 CCR) @ 700 ^oC	20.259	0.157
Sintered CaO (Sintering + 0 CCR) @ 800 ^oC	14.273	0.149

Effect of Reaction Temperature

To study the effect of reaction temperature, CaO reactions at 700 ^oC and 800 ^oC are conducted for comparison. Any parameters expect reaction temperature on CaO are fixed, therefore, temperature is the only factor in resulting CaO reactivity difference in the reactions. As can be seen in Figure 7 (a), the resulting CaO reactivity after the reactions at 700 ^oC is higher than that at 800 ^oC, where both reactivity results are tested at 650 ^oC. The corresponding morphological properties show the same trend. As stated above, CaO-CO_2 reaction is "in-ward diffusion mode", where non-structural CO_3^{2-} transfers back and forth through solid structure in the capture and release steps, while structural Ca^{2+} does not involve in the ionic transfer processes. Since product $CaCO_3$ has higher molar volume than solid reactant CaO[19], the product layer is expanded, and both the inner and surface pores are extruded during proceeding reactions[13,10,8,6]. New pores will be regenerated when O^{2-} leaves the solid layers. It is the properties of solid CaO and $CaCO_3$ that mainly determines the molar volume expansion-and-shrinking process rather than temperature. That is why CaO at 800 ^oC has higher resulting reactivity than that at 700 ^oC (see figure 7(a)).

Effect of Cyclic Gas-Solid Reactions

With both fixed the reaction temperature and reaction time, temperature-induced sintering effect difference on a solid particle could be ignored relatively. Cyclic gas-solid reaction effect is studied by comparing solid reactant CaO which goes through a cyclic reaction with the sample that only goes through the same temperature condition and time periods in the absence of reactive gases. As can be seen from Figure 7 (a), the resulting solid reactivity is deteriorated in the cyclic reactions and the deteriorating effect increases with increasing the number of carbonation-calcination cycles in the same reaction time. To eliminate the understanding that sintering causes the deteriorating effect on the product solid ($CaCO_3$), a product solid ($CaCO_3$) goes though the same temperature condition under CO_2 existence. As shown in Figure 7 (b), "Sintered $CaCO_3$" and "Sintered CaO" have the same reactivity which is higher than that of the "Sintering + 3 CCR". This comparison approves that the cyclic reaction is an independent factor which deactivates solid reactivity, which is against the understanding that solid deterioration was almost unanimously caused by the sintering effect in the previous studies[4,1,16,14,18]. When CO_2-capture occurs, volume expansion could remove the overall surface pores. Since the reaction of CaO and CO_2 does not contain structural ions diffusion, pore volumes at different sizes are squeezed down by molar volume expansion.

If the pore closing-and-opening process was not irreversible, reaction cycles would not influence the entire morphological properties in this case. Molar volume shrinking could generate pores all over the place on the solid surface during the CO_2-release reaction processes. New generated pores are usually small in size and they also occupy some space of previous large ones. As a result of that, bigger pores become smaller ones and the diameter of pores is decreasing in average (see Table 4). Due to the fact mentioned above, some inner pores which

are connected to CO_2 through surface pores at the beginning of the CO_2 capture step would be closed, and the connection would also be cut off during the continuous cyclic reactions. This mechanism is approved through the decreasing average pore-size of CaO in the experiments. As shown in Figure 8, with more carbonation-calcination reaction (CCR) cycles, the pore volume is significantly decreased in the 20-100nm pore diameter regions. However, they stay almost the same at very small pore diameter regions (smaller than 20nm).

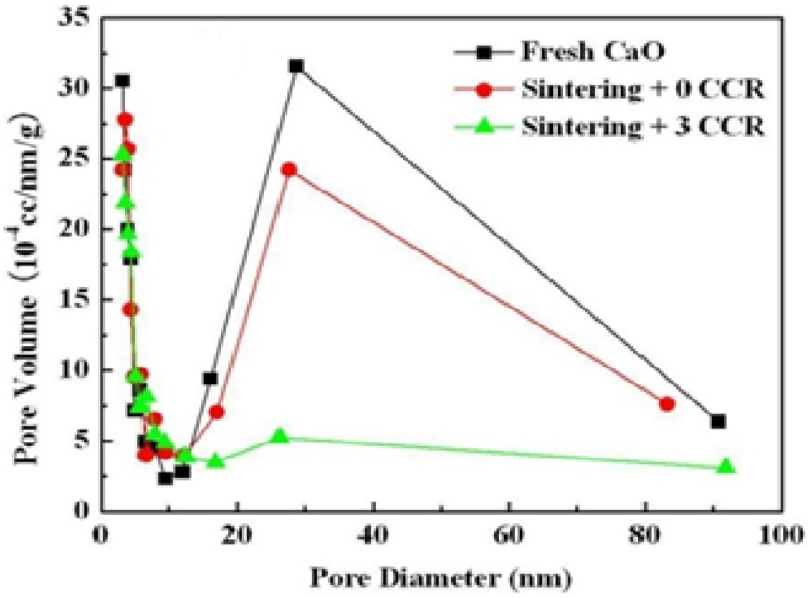

Figure 8: Pore size distributions of the tested CaO and Fe solids. (Negligible pore volume is present out of the displayed diameter ranges)

Table 4: Morphological information of the CaO solid reactants

Sample I.D.	Surface Area (m^2/g)	Pore Volume (cc/g)
Sintered CaO (Sintering + 0 CCR) @ 800 ^oC	14.273	0.149
Sintering + 3 CCR @ 800 ^oC	8.293	0.056
Sintered $CaCO_3$ @ 800 ^oC	15.800	0.130

Morphology analysis of the CaO samples

NOVA 4200e analyzer (Quantachrome Company) was used to test the CaO morphological properties. Surface area, pore volume, and pore size distribution were measured at -196 ^{o}C with Brunauer Emmett Teller (BET) and liquid N_2 was used as adsorbent.

Definition of the solid reactivity for gas capture

The solid's capture capacity is defined as weight capture percentage after 30 minutes' carbonation at 650 ^{o}C .

Equation 2: Weight Capture Percentage[19]

$$C_t = \frac{(W_t - W_o)}{W_0} \times 100(\%)$$

Where:

W_o: Sample weight after complete calcination/reduction. (mg)

W_t: Sample weight after 30 minutes' carbonation (for CaO)

On the basis of the definition of this parameter, a larger weight capture percentage C_t refers to a higher gas capture reactivity of a solid reactant.

Discussion

In the catalysis reactions, surface area and pore volume reflect the activity of a solid catalyst，and their conditions highly depend on their own preparation and reaction conditions. Various methods were tried in catalyst preparation process to improve the initial solid morphological properties. Thus, catalyst itself made from an ideal preparation process would not be converted through any chemical reactions. Therefore, extrinsic factors like sintering are the only reasons which could deteriorate the catalyst activity[5]. In a real process, such extrinsic factors could be ignored through improving preliminary solid condition，anti-sintering and reasonable reaction condition controls, from which making high quality and long-life catalyst morphological properties is feasible.

One of CaO reactant's intrinsic properties changes of CaO structure and surface morphological properties in cyclic reactions is ignored in previous researches. This cyclic structural change is a complex process which involves multiple factors in the cyclic reaction, such as the solid's inherent properties, solid-phase ionic transfer, and reaction conditions[19]. There are many factors affecting the cyclic structural changes. In the research stated above, solid morphological properties are deteriorated by the cyclic structural changes, which reveals that only optimizing the initial surface and pore volume is not enough in the cyclic reaction. One feasible method to get rid of CaO morphological deterioration is hydrating deactivated CaO sorbent during the CaO-CO_2 cyclic reactions[11]. However, some important properties like low mechanical strength are requested to the solid for this method, which restricts the applications of the properties.

Concluding remarks

In this study, we studied that CaO-CO_2 reaction is inward ionic diffusion mode, where non-structural ion CO_3^{2-} mainly dominate the overall ion transfers. Since CO_3^{2-} is very large size, the reaction of CaO-CO_2 is very slow. That is why the reaction was conducted for about 4 months. We also report the reactivity and morphological change of solid reactant CaO in the cyclic CaO-CO_2 reactions. Thermal Gravimetric Analysis (TGA) is used to analyze CaO's CO_2-capture capacity and surface area and pore structure from BET tests are conducted to characterize the CaO morphological properties. Effects of reaction temperature, reaction time, and cyclic reaction on the solid reactivity and morphological properties are independently examined. It is found that longer exposure to reaction temperature would decrease the surface areas, pore volumes, and corresponding reactivity of CaO, which is attributed to the extended sintering effect. Since cyclic carbonation-calcination reactions of CaO is non-structural ion diffusion (inward diffusion mode), a higher reaction temperature causes greater sintering, which aggravates CaO reactivity deterioration. With the effects of reaction temperature and reaction time excluded, the effect of a cyclic reaction is independently examined, which shows obvious deterioration to the solid reactants.

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